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NOVEL POLYETHYLENE COPOLYMERS

This invention relates to ethylene copolymers, and, more particularly, to copolymers of ethylene and certain acid comonomers.

It is an object of the present invention to provide new ethylene copolymers. A further object is to provide ethylene copolymers which are especially well suited for adhesive and coating purposes. Still another object is to provide new copolymers of ethylene with certain acid comonomers. Other objects will become apparent hereinafter.

The objects of the present invention are accomplished by a copolymer of ethylene and 0.1 to 10 weight % of an α-β ethylenically unsaturated acid having from 3 to 8 carbon atoms per molecule, and preferably by a copolymer containing from 1 to 8 weight % of the acid monomer, said copolymers having a melt index in the range of 0.01 to 30 g/10 min, as determined by ASTM D-1238-57 T.

The copolymers of the present invention combine superior adhesion, toughness, flexibility and printability with low permeability, high rigidity, stiffness and corrosion, solvent and moisture resistance. The surprising feature of the resins of the present invention is the increase of adhesion obtained in the range of comonomer concentrations stated combined with the retention of desirable properties of polyethylene, such as rigidity and solvent and moisture resistance. Additionally, the copolymers of the present invention can be readily handled at temperatures below their melting

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points, 110-120° C, at which they show little or no tendency to stick and can also be fabricated in standard polyethylene equipment. Thus, the resins of the present invention are extremely useful as adhesives, in such uses as the production of non-woven fabrics; as binders, in such uses as the preparation of laminates and as coating resins, in such uses as the coating of paper products.

Polyethylene homopolymers have low adhesive properties, poor printability and are not ordinarily suitable as adhesives or as laminating resins. However, the introduction of as little as 0.1 weight % of the acid comonomer, based on the copolymer, greatly increases the adhesion properties of the polyethylene. Acid component contents greater than about 10% do not significantly add to the adhesiveness or the printability of the copolymer. On the other hand, such increases in comonomer content cause those properties which are inherent in high molecular weight polyethylene and which are desirable in an adhesive to decrease. Acid comonomers such as are employed in the formation of the copolymers of the present invention act as telogens for the polymerization of ethylene, and, hence, if employed in high concentrations result only in low molecular weight products which do not have the toughness and flexibility, particularly at low temperatures, for which polyethylene is so well known. Additionally, the incorporation of acid comonomers in excess of 10 weight % causes an unacceptable decrease in the rigidity of the polymer product which rigidity is necessary, particularly in laminating

applications. Furthermore, the addition of more than 10 weight % of acid comonomer also causes a significant decrease in organic solvent resistance and moisture resistance which are highly desirable in an adhesive or in a coating resin. The greatly surprising feature of the copolymers of the present invention is that the introduction of the acid comonomer in the indicated concentrationsresults in a tremendous increase in adhesiveness combined with an unusually small decrease in the mechanical properties as compared to polyethylene.

Suitable acid comonomers are acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and the methyl and ethyl hydrogen maleates and fumarates. Of these, acrylic and methacrylic acid are preferred since they show the greatest ratio of increase in adhesiveness with retention of rigidity and solvent resistance.

Most ethylene copolymers with polar comonomers produced heretofore have been produced either in an aqueous system, at low pressures, i.e., up to 500 atmospheres, or in a batch process. However, these conditions do not result in the high molecular weight random, but homogeneous copolymers of the present invention. It will be readily recognized that in order to achieve high molecular weights in the copolymers of the present invention, it is necessary to employ polymerization conditions which result in high molecular

weight homopolymers of ethylene, since ethylene is the major component, particularly when considered on a molar basis. In view of the telogenic nature of the comonomer, however, it is not only necessary to employ conditions which result in high molecular weight polymers in the homopolymerization, but conditions which result in high molecular weight polymers in the presence of telogens. Conditions which result in high molecular weight copolymers wherein the acid component is a major constituent are readily available since as between the unsaturated acid and ethylene, the unsaturated acid is a substantially more active monomer which polymerizes more readily than ethylene and over a substantially wider range of conditions. The copolymerization of ethylene and the described unsaturated acids to result in high molecular weight copolymers, i.e., copolymers having a melt index in the range of 0.01 to 30 g/10 min, as determined by ASTM-D-1238-57T, wherein the ethylene content is at least 90% by weight requires high ethylene pressures of at least 1000 atmospheres, and, preferably from 1500 to 3000 atmospheres and a substantially telogen free (aside from the comonomer) single phase polymerization environment in which both monomers are soluble. Solvent systems which are suitable for the process comprise solvent systems heretofore used for polyethylene, such as benzene or ethylene itself which may be in liquid form or in vaporized form. Vaporized ethylene compressed to a density approaching that of liquid ethylene has essentially the solvent powers of liquid ethylene. Where the comonomer is not sufficiently soluble to allow a single phase polymerization suitable comonomer solvents are added. The

reaction temperature is in the range of 90° C to 280° C, and, preferably, in the range of 150° C to 240° C.

In order to achieve the hereinabove described increase of adhesion in combination with the retention of mechanical properties of polyethylene through the addition of the acid comonomer, it is essential to make a copolymer which contains the acid comonomer randomly dispersed throughout the entire polymer molecule in all molecules of the polymer, i.e., a random but homogeneous copolymer. In order to achieve such it is necessary, in addition to the aforementioned conditions, to employ a continuous polymerization process. Thus, it was discovered that the polymer forming reactivity of the unsaturated acid monomer is from 5 to 10 times that of the ethylene. Because of this substantial difference in reactivities, it is not only necessary to reduce the concentration of the comonomer in the feed in accordance with the reactivity ratio to obtain a copolymer of the desired acid content, but it is also essential to employ a continuous process in which the conversion of the ethylene to polymer, controlled by reactor residence time, is from 3 to 20%. By maintaining the feed ratio of ethylene to comonomer to the polymerization reactor in line with the reactivity ratio and limiting the polymerization of ethylene to its initial and fast polymerization, it is possible to obtain the random and homogeneous copolymers of this invention. In a batch process, the difference in reactivities of the comonomers results in a copolymerization in which polymers with a very high acid content are formed initially until the acid monomer is substantially used up, at which time the polymerization becomes substantially a homopolymerization of

polymers ranging all the way from unsaturated acid homopolymers to polyethylene and from randomly dispersed polymers to block copolym ers. On the other hand, the use of a continuous process under conditions above described results in an entirely different product, one which has very uniform comonomer distribution and is, therefore, substantially more homogeneous than the batch produced product.

In general, the polymerization of the comonomers is initiated by a free radical forming compound, such as oxygen, a peroxide or an azo-bis compound. Suitable peroxides include benzoyl peroxide, lauryl peroxide, t-butyl peracetate. A suitable azo initiator is azo-bis(isobutyronitrile). The quantity and preferred type of initiator is in accordance with the art established for the homopolymerization of ethylene.

The polymerization is preferably carried out in a stirred autoclave, stirred at high rates such as 250 rpm. Ethylene, the ethylene comonomer, which may be dissolved in ethylene or another suitable solvent, and initiator, also dissolved in a suitable solvent, are injected into the autoclave. The agitator is started and the feed is continued until the desired pressure is reached, at which time a discharge valve is opened to maintain the desired pressure. The temperature of the reactants is then built up to the "light off" state by any suitable means, such as for example, by the use of a heating jacket surrounding the autoclave, the use of internal or external electrical type heaters or the like. At these pressures and temperatures the reagents exist as a uniform phase. "Light off" occurs when the temperature is reached at which the polymerization initiator begins to generate free radicals at an appreciable rate. The free radicals induce the polymerization

of the monomers, and, since this reaction is exothermic, the temperature is observed to rise. When the temperature rises slightly the initiator produces free radicals at a faster rate and the exothermic polymerization of ethylene proceeds still faster. For this reason a marked temperature surge is observed as the reaction "lights off". Once "light off" is obtained, the application of heat through jackets into the reaction mixture and/or feed streams is discontinued. The reaction temperature, within narrow limits, is then maintained by controlling the amount of exothermic polymerization which also maintains a definite monomer to polymer ratio within the autoclave. In accord with the type of polymer, it is desired to produce, the temperature within the reactor is allowed to build up to the exact temperature that will produce that type of polymer. This is accomplished by regulating the concentration of initiator fed into the reactor. The exothermicity of the reaction and, therefore, the molecular properties of the polymer desired are therefore controlled by the amount of heating applied to the feed streams and the amount of initiator introduced. The resulting polymer stream is passed through a pressure let down valve into a vessel at substantially reduced pressure, but at the polymerization temperature, at which every reagent except the polymer is flashed off. The polymer is isolated and cooled to room temperature.

The synthesis of the resins of the present invention and basic properties of the resulting resins are further illustrated in Table I. The polymerization was carried out in a 2 liter autoclave. All reagent streams were maintained at temperature [illegible]. The initiator employed was t-butyl peracetate unless otherwise indicated. Ethylene was charged

to the reactor as a separate stream at a pressure of 1000 psig. Catalyst and comonomer were charged as separate streams as solutions in benzene. Indicated co-solvents were employed with those comonomers where solubility in benzene was difficult.

Table I

Run	Comonomer	Press. Atms.	Temp °C	Cat. Demand lb cat/1000# of polymer	Ethylene	Comonomer	Catalyst x 10^{-6}	Benzene	Cosolvent	Solvent/Total Monomer Ratio	Reactor Residence Time/min	Polymer Yield pph	Comonomer Content in wt.%	Melt Index g/10 min**	Stiffness psi***	Density g/cc****
		Reactor Conditions			Feed Streams in pph											
1	Ethy[illegible] Acid	1100	235	0.088	10	0.001	141	7.35	1.0(toluene)*	0.735	7.4	1.60	0.12	3.0-5.5	15,040	0.915
2	Ethylene [illegible] Acid	1200	238	0.0895	10	0.01	136	6.82	1.05 "	0.682	7.6	1.52	0.45	3.8-7.8	14,636	0.917
3	Ethy[illegible] Acid	1400	230	0.131	10	0.06	208	7.75	0.9 "	0.77	7.8	1.59	2.5	4.0-5.3	16,521	0.923
4	Ethy[illegible] Acid	1450	213	0.177	10	0.128	270	6.82	1.0 "	0.673	8.5	1.53	5.7	1.7-2.0	-	0.932
5	Eth[illegible]	1200	233	0.073	10	-		7.0	-		7.5	1.5	-	0.9-2.1	18,895	0.916
6	Ethyl[illegible] [illegible]lic Acid	1200	230	0.096	10	0.01	140	7.63	-	0.761	7.5	1.46	0.48	1.3-2.5	19,415	0.913
7	Ethyl[illegible] [illegible]ylic Acid	1200	231	0.108	10	0.02	163	7.75	-	0.772	7.5	1.49	1.18	4.4-5.2	19,294	0.915
8	Ethylen[illegible] [illegible]ylic Acid	1350	224	0.113	10	0.058	179	7.23	-	0.72	7.3	1.58	2.29	2.9-3.6	19,651	0.918
9	Ethy[illegible] [illegible]ylic Acid	1350	202	0.185	10	0.127	286	8.96	-	0.875	7.5	1.55	5.21	4.3-5.7	19,820	0.927
10	Ethy[illegible] Acid	1450	220	0.056	10	0.025	95	5.85	1.54(t-BuOH)	0.739	8.1	1.69	0.14	6.9-9.1	24,592	0.921
11	Ethy[illegible] Acid	1450	210	0.0826	10	0.0127	118	6.08	1.52 "	0.746	8.7	1.43	0.90	3.7-4.4	26,672	0.925
12	Ethyle[illegible] Acid	1350	220	0.224	10	0.01	331	8.36	-	0.835	7.6	1.48		4.7-7.8		
13	Ethy[illegible] Acid	1450	197	0.174	10	0.0096	226	5.34	1.33(MeOH)	0.67	8.5	1.30	0.76	5.8-7.4	29,457	0.928
14	Ethyle[illegible] Acid	1450	194	0.153	10	0.0188	221	4.67	0.99 "	0.56	8.9	1.45	1.06	3.7-5.8	26,456	0.928
15	Ethylen[illegible] Acid	1450	192	0.331	10	0.0584	542	4.9	0.926 "	0.86	8.9	1.64	3.14	5.5-9.9	32,725	0.934
16	Ethylen[illegible] [illegible]id	1450	182	0.484	10	0.111	788	4.52	1.46 "	0.546	9.2	1.63	5.29	3.6-7.6	34,558	0.942
17	[illegible] Acid	1400	199	0.205	10	0.02	297	8.18	-	0.815	8.0	1.45		2.11-3.0		
18	[illegible] Hydrogen Maleate	1200	226	0.152	10	0.0975	236	8.32	-	0.83	7.3	1.55	0.31	1.5-2.1	29,457	0.928
19	Ethyl[illegible] Hydrogen Maleate	1250	227	0.228	10	0.02	354	6.91	-	0.69	7.9	1.55	0.72	2.4-4.6	26,456	0.928
20	Ethyle[illegible] Hydrogen Maleate	1450	215	0.403	10	0.059	564	5.67	-	0.56	8.8	1.40	2.06	1.86-2.8	32,725	0.934
21	Ethyl[illegible] Hydrogen Male[illegible]	1450	195	0.460	10	0.120	685	5.50	-	0.545	9.0	1.49	3.84	6.3-6.8	34,558	0.942

* [illegible] polymerization to facilitate polymer purification

** [illegible]-57T

*** AS[illegible]-58T

**** D[illegible]

The surprising combination of properties obtained with the copolymers of the present invention is shown in the following table where the retention of desirable polyethylene properties such as stiffness is compared with the improvement in adhesive properties obtained with increasing concentrations of the acid comonomer.

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Table II

...mer	% Comonomer Content	Stiffness in psi	Elemendorf Tear in g/ml	Shore Hardness	% Ink Removed	Adhesion (gm/inch width) Aluminum	"Mylar", Polyester Film
Ethy... Acrylic	0.12	15,040	175	52(D)	95	-	-
Acid ...ymer	0.45	14,636	170	51(D)	-	1600	-
	2.5	16,525	227	52(D)	-	2500	-
	5.7	14,961	425	55(D)	0	2700	-
Eth... ...eth-	0.48	19,415	200	47(D)	100	-	-
Acry... ...id	1.18	19,294	210	49(D)	90	1400	-
Cop...	2.29	19,651	225	51(D)	-	2500	40
	5.21	19,820	406	50(D)	60	2700	60
Eth... ...ydrogen	0.31	20,754	209	-	60	-	-
Mal... ...polymer	0.72	20,252	180	-	60	1700	40
	2.06	24,473	192	-	15	1800	-
	3.84	24,424	197	-	0	1700	-
Eth... ...taconic	0.76	29,457	126	56(D)	65	670	-
A... ...ymer	1.06	26,456	147	57(D)	45	400	-
	3.14	32,725	151	59(D)	-	800	-
	5.29	34,558	167	61(D)	0	1600	400
Po... ...ne	0	18,895	233	50(D)	100	0	0

Stiffness was determined by ASTM D 747-58T. The Elemendorf Tear Strength and Shore Hardness are well known tests. The % ink removed was measured by the "Scotch Tape" test in which ink is applied to a film of the material, and after drying, scotch tape is applied to the inked material and then removed, the percentage of ink removed is calculated. Adhesion as measured by peel strength was obtained at a separation rate of 6"/min. The test samples were prepared by placing a 1 to 5 mil compression molded film of the acid copolymer between two layers of the foil to which adhesion was tested. The sandwich was placed in the jaws of the heat sealer to give a seal 1" x 4" at 250° C under 60 psi pressure with a dwell time of 0.15 seconds. The force required to peel the laminate was measured.

The novel ethylene copolymers of the present invention are useful as coating resins and as adhesives. They can be employed in the coating of cardboard, paper, metal foil, other plastic films such as ethylene terephthalate films and many other surfaces. They also are useful as laminating resins to bond such hydrocarbon polymers as polyethylene and polypropylene to the aforementioned substrates. In the adhesive field the copolymers of the present invention are particularly useful as binders for fibers.

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A. D. 2660

CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A copolymer of ethylene and an α-β ethylenically unsaturated acid having from 3 to 8 carbon atoms per molecule, said copolymer containing, based on the weight of the copolymer, from 0.1 to 10 percent of said acid and having a melt index of 0.01 to 30 g/10 min.

2. The copolymer as set forth in claim 1 wherein the acid content is from 1.0 to 8 percent.

3. The copolymer as set forth in claim 1 wherein the acid is acrylic acid.

4. The copolymer as set forth in claim 1 wherein the acid is methacrylic acid.

5. The copolymer as set forth in claim 1 wherein the acid is fumaric acid.

6. The copolymer as set forth in claim 1 wherein the acid is itaconic acid.

7. The copolymer as set forth in claim 1 wherein the acid is methyl hydrogen maleate.

8. The process of preparing a homogeneous, randomly dispersed copolymer of ethylene and an α-β ethylenically unsaturated acid having from 3 to 8 carbon atoms per molecule, said copolymer containing, based on the weight of the copolymer, from 0.1 to 10 weight percent of said acid and having a melt index of 0.01 to 30 g/10min, which comprises continuously charging ethylene, said acid and a free radical initiator into a reaction zone maintained at a pressure of 1000 to 3000 atmospheres and a temperature of 90 to 280° C. the ethylene

CLAIMS (continued)

and acid being charged in a ratio varying from 10000:1 to 100:2, converting from 3 to 20% of the ethylene to copolymer and continuously removing the resulting copolymer from the reaction zone.

9. The process as set forth in claim 8 wherein the temperature is from 150 to 240° C and the pressure from 1500 to 2000 atmospheres.

10. The process as set forth in claim 8 wherein the initiator is a peroxide.

11. The process as set forth in claim 8 wherein the polymerization is carried out in ethylene.

12. The process as set forth in claim 8 wherein the polymerization is carried out in benzene.

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SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente